JP, 3058342, and B [FULL CONTENTS]

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#### Notes:

- 1. Untranslatable words are replaced with asterisks (\*\*\*\*).
- 2. Texts in the figures are not translated and shown as it is.

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## FULL CONTENTS

# (57) [Claim(s)]

[Claim 1] After developing on a substrate a developing solution of amphiphile of a cation form which has bimolecular membrane organization potency, A manufacturing method of porous silica pellicle preparing multilayer bimolecular membrane pellicle of said amphiphile, contacting said multilayer bimolecular membrane pellicle in a solution containing a silica compound, and carrying out extraction elimination of said multilayer bimolecular membrane pellicle subsequently by removing a solvent from liquid membrane on said substrate.

[Claim 2]A manufacturing method of the porous silica pellicle according to claim 1 characterized for treatment which contacts multilayer bimolecular membrane pellicle of amphiphile in an acid further, and is again contacted in a solution of a silica compound after making a solution of a silica compound

contact by 1 time or carrying out repeatedly two or more times. [Claim 3]A developing solution which added a radical polymerization nature monomer to amphiphile of a cation form which has bimolecular membrane organization potency is developed on a substrate, After preparing multilayer bimolecular membrane pellicle of amphiphile which contains a radical

polymerization nature monomer by removing a solvent from liquid membrane on said substrate, Multilayer bimolecular membrane compound pellicle containing super-thin layer polymer which polymerized said radical polymerization nature monomer and constructed the bridge in two dimensions is formed, A manufacturing method of porous silica pellicle contacting a solution containing a silica compound to said multilayer bimolecular membrane compound pellicle, and carrying out incineration elimination of said multilayer bimolecular membrane compound pellicle subsequently.

membrane pellicle of amphiphile containing a radical polymerization nature monomer which polymerized is further contacted in an acid, A manufacturing method of the porous silica pellicle according to claim 3 characterized for treatment again contacted in a solution of a silica compound by 1 time or carrying out repeatedly two or more times.

time of earlying out repeatedly two of more times.

[Claim 4] After making a solution containing a silica compound contact, multilayer bimolecular

# [Detailed Description of the Invention]

[Industrial Application]

This invention relates to the method of manufacturing the porous silica pellicle of the multi-layer

construction which consists of a microfilm of a nano meter level.

[Description of the Prior Art]

Silica related compounds produced by the method using the silica gel of the porosity produced from sodium silicate and the phase separation nature of borosilicate glass, the sol-gel method, etc., such as porous glass and a stratified poly-silicic-acid salt, use the vesicular structure, and are used in fields, such as substance separation and catalyst support.

In uses, such as substance separation and catalyst support, it is required to enlarge the amount of penetrations of release material or reacting matter. Then, it is required that a film should be produced to the film-like pellicle which maintained film strength, moreover made thickness thin, and lowered film strength. When demonstrating the operation resulting from the pore structure of pellicle effectively, it is required that pore structure should be controlled by a nano meter level.

However, since the many of the conventional silica related compound raw material are powdered, it is granulation-made hard to pellicle-ize and it is used in the status that it fabricated to grain form, tabular, massive, etc.

For example, in the typical sol-gel method which pellicle-izes silica, the silica film is produced by applying the hydrolysis solution of an alkoxysilane substance on a substrate, and forming a gel coating film by heat-treatment etc. However, when manufacturing a silica film with a sol-gel method, in connection with the crosslinking reaction by evaporation of a solvent, or generation of a siloxane bond (Si-O-Si), volume shrinkage arises at the time of thin film forming. Therefore, the pellicle obtained by being easy to generate a crack has a weak structure. It is dramatically difficult actually to manufacture film-like pellicle from this point.

Since the mechanical strength which is equal to the adhesion of a coating film, a substrate, etc. and the volume shrinkage at the time of film formation is required of a substrate, a supporting lamella, etc. when using a substrate, a supporting lamella, etc., restrictions are added to the quality of the material of a substrate, a supporting lamella, etc. In the case of silica coating membrane, a porous body is used from the purpose use of the pellicle obtained also as a substrate, a supporting lamella, etc. However, it originates in the pore structure of this porous body, and the pellicle which has uniform thickness especially by the microfilm of a submicron level is hard to be obtained.

Since the silica film produced with the sol-gel method is a three-dimensional bridging body, the obtained pellicle has formless pore structure.

[Problem(s) to be Solved by the Invention]

Thus, when based on a method, a sol-gel method, etc. which fabricate the conventional powder, it was difficult to manufacture the porous silica pellicle of the shape of a film which can enlarge the amount of penetrations of release material and reacting matter suitable for the purpose uses, such as substance separation and catalyst support. Especially the thing for which thickness is controlled by the precision of a nano meter level was impossible.

Then, in order that this invention persons may moreover lower membrane resistance about the manufacturing method of a film-like silica film, maintaining film strength, they inquire wholeheartedly about the method of making thickness thin, and came to complete this invention.

about the method of making thickness thin, and came to complete this invention. That is, in this invention, the character in which a certain kind of amphiphile forms a molecular level and the multilayer bimolecular membrane pellicle which has high regularity on a nano meter level if it puts in another way is used.

Therefore, it aims at manufacturing the silica film which controlled pore structure by the nano meter

### level.

[The means for solving a technical problem]

In this invention, after developing the developing solution of amphiphile with bimolecular membrane organization potency on a substrate, the multilayer bimolecular membrane pellicle of amphiphile is prepared by removing a solvent from the liquid membrane on a substrate. And this multilayer bimolecular membrane pellicle is contacted in the solution containing a silica compound, and a silica compound is made to permeate that pore opening by using multilayer bimolecular membrane pellicle as a mold. Subsequently, a film-like silica film is manufactured by carrying out extraction elimination of the amphiphile with an organic solvent if needed.

Or after contacting multilayer bimolecular membrane pellicle in a silica compound content solution, the silica compound of the specified quantity can also be made for the treatment which makes an acid contact succeedingly and is again contacted in a silica compound content solution to permeate 1 time or by repeating two or more times.

The amphiphile used by this invention is a compound which has both a polar group and a hydrophobic group simultaneously in the same intramolecular.

As a polar group, the combination of the polyols containing sulfonate, sulfate, ammonium salt, polyamine salt, carboxylate, a sulfonyl salt, phosphate, phosphonate, a phosphonium salt, polyether, alcohols, and sugar residues and these groups can be used. However, when taking reactivity with a silica compound into consideration, what is an ion pair type like ammonium salt, and has especially a cationic residue, for example is preferred.

On the other hand, as a hydrophobic group, the combination of an alkyl group, an alkyl allyl group, an alicycle group, condensed multi-ring groups, and these groups can be used. However, when forming stable bimolecular membrane as well as a biomembrane, a certain specific partial chemical constitution is required. For example, it is alkyl \*\*\*\*\*\* including \*\*\*\* segments, such as two or more alkyl length chains or azobenzene, and biphenyl. Since the feature and a Reason the thin-film-forming ability by this is high, a typical example of a compound, etc. on the chemical constitution of the amphiphile which takes this point and a bimolecular membrane structure are explained to Tokuganhei1-58889 in detail, it omits here.

In the amphiphile of the specified quantity, it dissolves or distributes and the developing solution of amphiphile is prepared by the solvent. As a solvent, in many cases, water is used, but use of an organic solvent is also possible.

A glass substrate, quartz plate, fluoro pore, graphite slab, silicon substrate, precise polymer film, and porosity polymer film etc. are among the substrates with which a developing solution is developed. To the surface of a substrate, hydrophilization treatment or hydrophobing treatment may be performed according to the kind of developing solution. For example, it is also effective to carry out hydrophilization treatment of a part of substrate face, and to carry out hydrophobing treatment of the remaining surface portions so that a developing solution may be developed by the predetermined area on a substrate face.

If a solvent is removed from the developing solution developed on the substrate, amphiphilic bimolecular membrane pellicle will be formed. In order to secure the regularity of the molecular assembly of amphiphile in the process in which this solvent is removed, it is preferred to remove a solvent gradually. Although based also on the solvent system of a developing solution, if the conditions

of solvent elimination show an example in the case of an aqueous solution system, they will be performed within the homoiothermal constant humidity layer set as 25 \*\* near a room temperature, and 60% of relative humidity, applying three days. At this time, the thickness of the multilayer bimolecular membrane pellicle of the amphiphile adjusted is decided by the surface area of the substrate developed, the concentration of the amphiphile in a developing solution, the volume of a developing solution, etc., and the thickness of the silica film finally manufactured is also decided.

Even if it removes the multilayer bimolecular membrane pellicle of the amphiphile obtained after removing a solvent from a substrate, it holds free-standing [ sufficient ]. However, when taking operativity into consideration, it is preferred to perform contact treatment, such as immersion to a silica compound content solution, to the multilayer bimolecular membrane pellicle adhering to a substrate.

The silica compound in this invention refers to the compound which mainly has Si-O binding. As for the solution containing this silica compound, when taking into consideration the solubility over the organic solvent of the multilayer bimolecular membrane pellicle of amphiphile, it is preferred that it is an aqueous solution system. In order to raise the solubility of a silica compound, the silica compound content solution which adjusted the solution to acidity or basicity can also be used. Although potassium silicate, sodium silicate, colloidal silica, etc. are illustrated as an usable silica compound by this invention, it is not limited to in particular these.

As for a silica compound content solution, viscosity becomes high as the concentration of a silica compound becomes high. Therefore, while carrying out immersion neglect of the multilayer bimolecular membrane pellicle, it originates in evaporation of a solvent, the gelling film of a silica compound is formed in the solution surface, and handling may become difficult. Then, it is appropriate to make concentration of a silica compound into 1 to 15weight % of the range.

The immersion time of the multilayer bimolecular membrane pellicle to a silica compound content solution becomes settled by the ion exchange reaction nature of the amphiphile in the multilayer bimolecular membrane pellicle mentioned later, and a silica compound. Although the reaction of amphiphile and a silica compound has some merits and demerits according to the kind of amphiphile in multilayer bimolecular membrane pellicle, in many cases, it is ended within about 12 hours in 1 to 15weight % of the silica concentration range at the room temperature of around 20 \*\*. Therefore, immersion treatment is enough if it gives in time beyond this.

The multilayer bimolecular membrane pellicle of the amphiphile which carried out immersion treatment to the silica compound content solution is washed with water, and after drying, extraction elimination of the amphiphile is carried out by making the organic solvent selected according to the kind of amphiphile into extractant. Amphiphile is removed by this treatment and the silica film of the shape of a multilayer film which consists of a microfilm of a nano meter level is obtained.

The obtained silica film has large surface area, as the below-mentioned embodiment shows, and it has a vesicular structure. However, since the thickness of a film is very small, free-standing may be missing or it may bit-ize. Then, this invention persons examined how to manufacture the silica film of the existing shape of a free-standing film, by promoting growth of the silica film in a stratification plane. [ as a result the multilayer bimolecular membrane pellicle of the amphiphile which carried out immersion treatment to the silica compound content solution ] After making it wash and dry, the treatment which is contacted in an acid and is again immersed in the solution of a silica content compound 1 time or the method of repeating two or more times, Or the radical polymerization nature monomer was added to the developing solution which prepares amphiphilic multilayer bimolecular membrane pellicle, and it found

out that the method of using the multilayer bimolecular membrane pellicle containing the super-thin layer polymer prepared by carrying out polymerization of this monomer in multilayer bimolecular membrane pellicle, etc. were effective.

For example, in adopting acid treatment, after washing and drying the multilayer bimolecular membrane pellicle which carried out immersion treatment to the silica compound content solution, treatment contacted with the gas of an acid, an aqueous solution, or its steam is performed. And after washing and drying, multilayer bimolecular membrane pellicle is again immersed in a silica compound content solution. If 1 time or the organic solvent which gave repeatedly two or more times and was finally chosen according to the kind of amphiphile is made into extractant for this the treatment of a series of to the multilayer bimolecular membrane pellicle of amphiphile and extraction elimination of the amphiphile is carried out, The silica film of the shape of a film provided with free-standing is manufactured to such an extent that pincettes can fully be dealt with.

The halide acid in which in many cases the acid used contains the halogen anion since the kinds for an anion of the amphiphile of a cation form are halogen anions, such as chlorine, bromine, and iodine, is recommended. However, other acids, such as sulfuric acid, nitric acid, phosphoric acid, and carboxylic acid, can also be used.

It is also effective to be a gas-like or to expose to the steam of aqueous solutions, such as hydrochloric acid, for example like hydrochloric acid, as a contact method for the multilayer bimolecular membrane pellicle of the amphiphile processed with the silica compound content solution, when the vapor pressure of an acid is high. However, the method of immersing multilayer bimolecular membrane pellicle in the aqueous solution of an acid is simple, and, moreover, effective.

Although the acid concentration in particular of an aqueous solution is not restricted, about 0.1-1M is preferred for it from the field of the ease of dealing with it. a reaction ends this immersion treatment like the treatment which uses a silica compound content solution in the density range of 0.1-1M -- if there are 12 hours or more, it will come out enough.

Treatment by the silica compound content solution performed by continuing at acid treatment can be performed under the same conditions as treatment by the silica compound content solution in a previous process.

A series of operations including acid treatment can be repeatedly performed to the multilayer bimolecular membrane pellicle of amphiphile. Although the number of cycles at this time changes a little with kinds of amphiphile which constitutes multilayer bimolecular membrane pellicle, the effect of repetition treatment may be saturated with 2 to 5 times or more. Thus, free-standing [ of the obtained silica film ] improves by carrying out contact treatment of the multilayer bimolecular membrane pellicle of amphiphile to a silica compound content solution and an acid by turns.

The amphiphile which has bimolecular membrane organization potency can incorporate a radical polymerization nature monomer in multilayer bimolecular membrane pellicle, as Tokuganhei1-58885 showed. The incorporated radical polymerization nature monomer forms the microfilm layered product which constructed the bridge in two dimensions. Then, it is possible also by using this microfilm layered product to manufacture the silica film of the shape of a film provided with free-standing.

That is, after developing on a substrate the developing solution which added the radical polymerization nature monomer to the amphiphile of the cation form which has bimolecular membrane organization potency by the same method, a solvent is evaporated and the amphiphilic multilayer bimolecular membrane pellicle containing a monomer is prepared. And the radical polymerization nature monomer

contained in multilayer bimolecular membrane pellicle is polymerized by thermal polymerization, photopolymerization, radiation polymerization, etc., and the multilayer bimolecular membrane compound pellicle containing the super-thin layer polymer which constructed the bridge in two dimensions is obtained. Immersion treatment to a silica compound content solution or immersion treatment to the silica compound content solution which combined acid treatment is similarly performed to this compound pellicle, and a silica film is manufactured. At this time, the immersion treatment and acid treatment to a silica compound content solution can be performed under the same conditions as the multilayer bimolecular membrane pellicle prepared from the developing solution which does not contain a radical polymerization nature monomer.

Although the method of preparing the multilayer bimolecular membrane compound pellicle which polymerizes the radical polymerization nature monomer used and this monomer, and contains super-thin layer polymer is shown by Tokuganhei1-58885, other monomers and methods of preparation can also be adopted without being restrained by it. If an example of a radical polymerization nature monomer is shown, it can also be used making independent or the plurality of polyfunctional monomer of a following formula copolymerize. R in a following formula shows CH<sub>3</sub> or H.

$$\begin{array}{c} R \\ CH_{2} = CCOO & (CH_{2}CH_{2}O)_{n}COC = CH_{2} \\ & (n = 2 \sim 2 \, 0) \\ CH_{2} = CCOO & (CH_{2}CHCH_{2}O)_{n}COC = CH_{2} \\ CH_{2} = CCOO & (CH_{2}CHCH_{2}O)_{n}COC = CH_{2} \\ R \\ R \\ CH_{2} = CCOO & (CH_{2})_{n}OCOC = CH_{2} \\ CH_{2} = CCOO & (CH_{2})_{n}OCOC = CH_{2} \\ CH_{2}OCOC = CH_{2} \\ CH_{3}CH_{2} - C - CH_{2}OCOC = CH_{2} \\ R \\ CH_{2}OCOC = CH_{2} \\ R \\ CH_{2}OCOC = CH_{2} \\ R \\ \end{array}$$

Diluents, such as a monofunctional monomer, ethylene glycol, glycerol, are also mixable to these polyfunctional monomer. The following are illustrated as an usable monofunctional monomer.

Finally the multilayer bimolecular membrane compound pellicle in which treatment by a silica compound content solution etc. was performed turns into a silica film in response to heat treatment under an oxidizing atmosphere. Specifically, incineration elimination of amphiphile and the super-thin layer polymer is carried out by heating multilayer bimolecular membrane compound pellicle at not less than 300 \*\* with an electric furnace etc. by oxygen gas flowing down under air. [For \*\*]

A certain kind of thing forms the molecular assembly which has the same bimolecular membrane structure as a biomembrane among the amphiphile which has a polar group and a hydrophobic group in the both ends of a molecule. It can not only be obtained as a water dispersing element, but after the amphiphile which forms this bimolecular membrane develops the water dispersion of amphiphile on a solid board, it can fabricate it by removing water gradually to the multilayer bimolecular membrane pellicle of the shape of a film with free-standing [ of transparency ]. And the regular bimolecular membrane structure of amphiphile is maintained in the multilayer bimolecular membrane pellicle of the shape of an acquired film, and taking the high lamella structure of two-dimensional smoothness is known [for example, Thin Solid Films, 121, and L89 (1984) reference]. On the other hand, shaping of the pellicle which there is free-standing and has a structure of a regular molecule organization with amphiphile without bimolecular membrane organization potency, i.e., a common surface active agent, is difficult.

Then, especially this invention person pays his attention to regular organization highly with the molecular level of the multilayer bimolecular membrane pellicle prepared from the amphiphile which has bimolecular membrane organization potency, When using as a mold high lamella structure of the two-dimensional smoothness which amphiphile makes and forming a silica layer, I thought that the silica film which consists of a microfilm of a molecular level, i.e., a NANOMETA unit, was obtained by

the shape of a film. Here, the amphiphile of an ion pair type [hydrophilic part] has ion exchange nature in a counter ion, and the ion exchange of it is carried out easily, maintaining organization. It tried to between [layers] ize a silica compound to the hydrophilic part of multilayer bimolecular membrane pellicle using this character. Since the silica compound which generally consists of Si-O binding was anionic, the cationicity type was chosen as amphiphile.

The ion exchange reaction between amphiphile and a silica compound advances almost stoichiometrically, and between the hydrophilic part layers of amphiphile is filled with a silica compound. And if extraction elimination of the amphiphile is finally carried out with a suitable organic solvent, the silica film which consists of a microfilm of a NANOMETA unit will be obtained by the shape of a film.

At this time, by an ion exchange reaction, it originates in the difference in the molecule cross-section area of a silica compound and amphiphile, etc. between[layers ]ized, and between the layers of multilayer bimolecular membrane pellicle may not fully be filled with a silica compound. In such a case, since the silica film obtained after extracting amphiphile is too thin, there may be free-standing [no] or it may bit-ize. Then, it is necessary between the layers of multilayer bimolecular membrane pellicle to introduce a lot of silica compounds.

For introduction of this silica compound, in this invention, it is treatment by an acid and activation of the ion exchange site is carried out into multilayer bimolecular membrane pellicle. In order that the anionic silica compound by which interlamellar introduction was carried out by ion exchange may be protonated by acid treatment, may be carbonated and may keep neutrality electric, the opposite anion of an acid processed in multilayer bimolecular membrane pellicle is introduced again, and an ion exchange site carries out activation of it. By repeating this treatment, a lot of silica compounds beyond stoichiometry can be between [layers ]ized to multilayer bimolecular membrane pellicle. However, a limit is among the quantity of the silica compound introduced, and it may be saturated to a number of cycles. Although this cause is not certain in a present stage, it is imagined to be that in which spatial restrictions of the hydrophilic part of multilayer bimolecular membrane pellicle originate.

In the multilayer bimolecular membrane compound pellicle of the amphiphile containing the super-thin layer polymer prepared by carrying out polymerization of the radical polymerization nature monomer, the organization of amphiphile with comparable high regularity is formed as compared with the multilayer bimolecular membrane pellicle prepared only from amphiphile. This is clear from experimental results, such as an X diffraction, as shown in Chem.Lett. and p2059-2062 (1989). When the multilayer bimolecular membrane compound pellicle containing super-thin layer polymer is used, super-thin layer polymer acts as a binder of the silica compound introduced by ion exchange, and is imagined to promote the layer planum growth possibility of the silica compound under oxidation treatment.

treatment.

[Example]

Hereafter, an embodiment explains this invention concretely.

- Embodiment 1- The compound with the structure of a following formula (1) was used as amphiphile which has bimolecular membrane organization potency.

$$CH_3 - (CH_2)_{-1} O - (CH_2)_{-1} N^+ (CH_3)_{-1} Br^- \cdot \cdot \cdot \cdot (1)$$

Pure water was made to distribute this amphiphile (1), and the developing solution of 20mM was prepared. [by developing the obtained developing solution on the fluoro pore (this is only hereafter

called fluoro pore) enclosed by the acetic acid cellulose film frame, and holding a developing solution for three days under the atmosphere of the temperature of 25 \*\*, and 60% of relative humidity in the status as it is ] The moisture in a developing solution was evaporated and yellow multilayer bimolecular membrane pellicle was obtained by the existing free-standing translucency.

After immersing the produced multilayer bimolecular membrane pellicle in the potassium silicate aqueous solution diluted to 10weight % and neglecting it for 12 hours, it took out from the aqueous solution. The multilayer bimolecular membrane pellicle after treatment presented the status that it swelled a little. This multilayer bimolecular membrane pellicle carried out extraction elimination of the amphiphile (1) by being immersed in a methanol solvent, after washing enough and drying with pure water subsequently.

The obtained silica film was a film which is about 10 micrometers of transparent white thickness which has brittleness a little. When this silica film was observed with the scanning electron microscope (SEM), that fine structure was a multilayer film structure which consists of a microfilm of nano meter order of magnitude. The surface area of the silica film calculated from the amount of nitrogen absorption was  $260\text{m}^2/\text{g}$ .

- Embodiment 2- The compound with the structure of a following formula (2) was used as amphiphile with bimolecular membrane organization potency.

$$CH_3 - (CH_2)_{15} OOCCHNHCO - (CH_2)_{10}N^+ (CH_3)_3B_x^ CH_3 - (CH_2)_{15} OOC - (CH_2)_2$$
 $\cdot \cdot \cdot \cdot \cdot (2)$ 

20mM moisture powder developing solution prepared from this amphiphile (2) was developed on the fluoro pore, moisture was evaporated under the same conditions as Embodiment 1, and the multilayer bimolecular membrane pellicle of translucency was produced.

The obtained multilayer bimolecular membrane pellicle was immersed in the potassium silicate aqueous solution diluted to 10weight %, and was processed like Embodiment 1. The obtained silica film was a white bit.

Then, after the multilayer bimolecular membrane pellicle of amphiphile (2) was immersed in the potassium silicate aqueous solution, immersion treatment was carried out to the hydrobromic acid aqueous solution of 0.2M for 12 hours, the operation again immersed in a potassium silicate aqueous solution for 12 hours was repeated 3 times, and, finally extraction elimination of the amphiphile (2) was carried out with methanol solution. As a result, the existing shape of a free-standing film was fully presented, and the silica film whose thickness is about 30 micrometers was obtained.

When the section of this silica film was investigated by SEM, the multilayer film structure with which the microfilm of several nanometer unit was located in a line in parallel with the film plane of a silica film as shown in Fig. 1 was observed. The surface area calculated from the amount of nitrogen absorption was  $210\text{m}^2/\text{g}$ .

- Embodiment 3- The compound shown in a following formula (3) was used as amphiphile with bimolecular membrane organization potency.

$$CH_3 - (CH_2)_{11}OOCCANHCO - O + (CH_2)_4 N^+ (CH_3)_3 B_r^- \\ CH_3 - (CH_2)_{11}OOC - (CH_2)_2 \\ \cdot \cdot \cdot \cdot (3)$$

The moisture powder developing solution of 50mM prepared from this amphiphile (3) was developed on

the fluoro pore, moisture was evaporated like Embodiment 1, and white multilayer bimolecular membrane pellicle was obtained by translucency.

To the produced multilayer bimolecular membrane pellicle, it replaced with potassium silicate of Embodiment 2, the 10 weight % aqueous solution of sodium silicate was used, the treatment immersed every 12 hours the hydrobromic acid aqueous solution of 0.2M and by turns was repeated 4 times, and extraction elimination of the amphiphile (3) was carried out with the methanol solvent at the last. The obtained silica film had the shape of a white film with free-standing. The surface area of the silica film calculated from the amount of nitrogen absorption was  $200\text{m}^2/\text{g}$ .

- Embodiment 4-, [ amphiphile (2) ] [ 20mM water dispersion which pure water was made to distribute ] 2-mol% of 4 (2-hydroxy ethoxy) phenyl-(2-hydroxy ethoxy-2-propyl) ketone was mixed to 2 organic-functions monomer (4) and the polymerization initiator of amphiphile (2) and an equimolecular amount, and the developing solution was adjusted. After developing this developing solution on the fluoro pore and evaporating moisture like Embodiment 1, UV irradiation was carried out with the very-high-pressure mercury lamp, and crosslinking polymerization of the 2 organic-functions monomer (4) was carried out.

$$\begin{array}{ccc}
O & O & O \\
\parallel & \parallel & \parallel \\
CH_2 = CHCO (CH_2CH_2O)_nCCH = CH_2 & \cdots & (4) \\
& n = 1 4
\end{array}$$

Immersion treatment of the multilayer bimolecular membrane compound pellicle of the shape of a produced bright film was carried out to the potassium silicate aqueous solution like Embodiment 1. And after making it wash and dry with pure water, it supplied to the core box electric furnace, the rise in temperature was carried out by a part for heating-rate/of 10 \*\*, and it was neglected at 500 \*\* for 10 hours.

The obtained silica film has free-standing [enough], and was presenting the shape of a translucent film. Although the surface area of this silica film suited a little low trend by 170m<sup>2</sup>/g, in observation of the film section by SEM, the multilayer film structure which consists of a nano meter order-of-magnitude microfilm was accepted.

- Comparative example - The silica film was prepared with the sol-gel method which used alkoxysilane as the starting material. That is, after adding the 0.05N dilute-hydrochloric-acid aqueous solution of ten weight sections as alkoxysilane Si(OCH<sub>3</sub>) 4 of 20 weight sections, and an object for a hydrolysis and

agitating for 1 minute to ethanol 50 weight section, it was developed and neglected on the glass petri dish. Most solvents evaporated behind one whole day and night, and the developing solution became a water-white very weak silica flake. When the section is observed by SEM, it has the fine structure which is [as / show / in Fig. 2] featureless. The surface area calculated from the amount of nitrogen absorption also showed the low value below  $1\text{m}^2/\text{g}$ .

# [Effect of the Invention]

After using the unique structure of the bimolecular membrane aggregate which amphiphile forms in this invention and making a silica compound contain between the layers of multilayer bimolecular membrane pellicle as explained above, extraction elimination of the amphiphile is carried out with the proper solvent. Thus, since the produced silica film is formed considering the multilayer bimolecular membrane structure of amphiphile as a mold, structure control of it is carried out by nano meter order of

magnitude, and it becomes what has dramatically big surface area. Since it has free-standing, the handling of a silica film is also easy. Therefore, when using this silica film as a substance demarcation membrane, catalyst support, etc., it originates in that big surface area, and is used as a highly efficient material

[Brief Description of the Drawings]

<u>Fig. 1</u> is a SEM photograph in which the multi-layer construction of the silica film produced in Embodiment 2 is shown, and Fig. 2 is a SEM photograph in which a precise structure without the feature of the silica film produced by the sol-gel method of the comparative example is shown.



[Fig. 2]



1.00µm

[Translation done.]